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(21) International Application Number: PCT/US83/00636 (22) International Filing Date: 4 May 1983 (04.05.83) (71) Applicant: GENERAL ELECTRIC COMPANY [US/ US]; 1 River Road, Schenectady, NY 12305 (US). (72) Inventors: VAN ABEELEN, Petrus, Cornelis, Aloysius, Maria ; Haakbus 10, NL-5126 WN Gilze & Ryen (NL). BUSSINK, Jan ; Olympianlaan 20, NL-Bergen op Zoom (NL). HEUSCHEN, Jean, Marie, Hubert ; Konijnenberg 13, NL-4661 HA Halsteren (NL). (74) Agents: KING, Arthur, M.; International Patent Opera- tion, General Electric Company, 570 Lexington Ave- nue, New York, NY 10022 (US) et al. (81) Designated States: AU, DE (European patent), FR (Eu- ropean patent), GB (European patent), JP, NL (Euro- pean patent).		Published <i>With international search report.</i>
(54) Title: HIGH IMPACT, HIGH MODULUS FIBER REINFORCED LINEAR POLYESTER (57) Abstract High impact, high modulus thermoplastic molding compositions comprising: (a) a linear polyester; (b) a fibrous reinforcing agent essentially free of any sizing agent; and (c) a small amount of a polysiloxane having a substantial content of Si-H bonds.		

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HIGH IMPACT, HIGH MODULUS FIBER
REINFORCED LINEAR POLYESTER

This invention is directed to an improved linear polyester composition in intimate admixture with an unsized fibrous reinforcing agent and a small amount of a hydrogen siloxane.

BACKGROUND OF THE INVENTION

Incorporating fibrous reinforcements, such as glass fibers and rockwool fibers, into various resins is known to improve dimensional stability, heat distortion temperature, creep resistance, tensile strength and, most dramatically, elastic modulus. However, this always results in a serious deterioration in overall ductility, manifested in poor notched and unnotched impact strength as well as a decreased falling ball impact strength. Even small amounts of fibrous reinforcements have a serious effect on the ductility of polyesters. If it is sought to improve impact performance by adding conventional impact modifiers, such as selectively hydrogenates styrene-butadiene-styrene block copolymers, then there is a detrimental effect on stiffness (modulus) and only a minor improvement in impact strength, in any event. It has been found that elimination of the adhesive bond between the polyester and the fibrous reinforcing agent can be accomplished by burning off or otherwise using fibers free of conventional sizing or coupling agents. This does improve ductility, but only for relatively low fiber contents, e.g., up to less than about 10% by weight of sizing-free glass fibers in the polyesters. This is usually below the optimum amount.

It has now been discovered that the addition of poly C₁-C₁₀ alkyl (or phenyl) hydrogen siloxanes to compositions comprising "pristine" (or sizing-free fibrous reinforcements and polyester, in which the fiber content

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exceeds even 30%, results in a tremendous improvement in falling ball (ductile) impact strength, and notched impact and unnotched impact strengths, too. These can be improved by several hundred percent with almost full retention of the elastic modulus.

It is believed that the following conditions are essential herein:

(i) sizing agents (on the fibrous reinforcement or separately added) must be absent because these either evoke adhesive bonds between the matrix and fiber, or they prevent reactions between the hydrogen polysiloxane and the fiber, or both;

(ii) a very good dispersion of the fibers in the matrix is required;

(iii) for best combination of high modulus and creep performance, the addition of polysiloxane is preferably kept below 1.0% and, especially preferably, below 0.5%; and

(iv) the polysiloxane used must contain hydrogen silicon bonds.

Following the use, especially, of short glass fibers, additional advantages in improved isotropy and high surface quality are obtained. It is again reemphasized, that sizing agents must not be present to contribute to adhesive bonds between matrix and fibers, nor should they prevent reactions between the silicon-hydrogen bond-containing polysiloxane and the fibers. In practical terms this means that pristine fibers should be used. Using the factors mentioned above, the falling dart impact strength of a 20% short glass fiber-reinforced polyesters can be increased from <5J to 60G, while the unnotched impact bar increases from 350 to 950 J/m. The new composition has a desirable high modulus. These results are evident at surprisingly low levels of hydrogen polysiloxane. Substantially the same results are also

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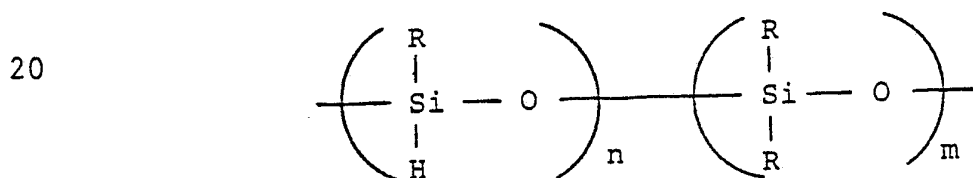
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obtained with other fibrous fillers, pristine or virgin, including rockwool-mineral fibers, carbon fibers, and the like.

SUMMARY OF THE INVENTION

5 According to the present invention, there are provided high impact strength, high modulus thermoplastic compositions comprising per 100 parts by weight (a), (b) and (c), an intimate admixture of:

- 10 (a) from about 95 to about 35 parts by weight of a linear polyester polymer or copolymer;
- (b) from about 5 to about 65 parts by weight of a fibrous reinforcing agent essentially free
- 15 of any sizing agent; and
- (c) from about 0.05 to about 4 parts by weight of a hydrogen siloxane comprising units of the formula



25 wherein R is hydrogen, C₁-C₁₀ alkyl, phenyl or a mixture of any of the foregoing, and n plus m is at least 4, and, for example, up to about 200.

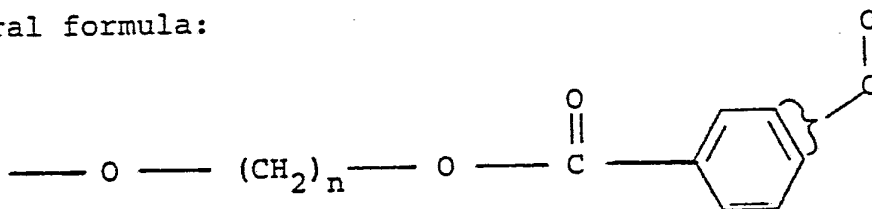
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DETAILED DESCRIPTION OF THE INVENTION

The linear polyesters (a) used in the practice of the present invention are polymeric glycol esters of terephthalic and isophthalic acids. They are available commercially or can be prepared by known techniques such as by the alcoholysis of esters of the phthalic acid with a glycol and subsequent polymerization, by heating glycols with the free acids or with halide derivatives thereof, and similar processes. These are described in U.S. Patent Nos. 2,465,319 and 3,047,539.

Although the glycol portion of the polyester can contain from two to ten carbon atoms, it is preferred that it contain from two to four carbon atoms in the form of linear methylene chains.

Preferred polyesters will be of the family consisting of high molecular weight, polymeric glycol terephthalates or isophthalates having repeating units of the general formula:



wherein n is a whole number from two to four, and mixtures of such esters, including copolyesters of terephthalic and isophthalic acids.

Especially preferred polyesters are poly(ethylene terephthalate) and poly(1,4-butylene terephthalate).

Conventional additives, such as anti-static agents, pigments, mold release agents, thermal stabilizers, and the like can be present in component (a).

The fibrous reinforcing agent (b) can vary widely in nature and type, so long as it is "pristine", that is, essentially free of any sizing materials, as mentioned above. There can be used glass fibers, mineral fibers, such as rockwool, asbestos, and the like, carbon fibers, and others.

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Preferred are glass fibers and rockwool fibers.

The length of the filaments, whether or not they have been bundled to form fibers, should be between about 50 mm and 6 mm, for long fibers and between about 6 mm and 0.05 mm in the case of short fibers. Alkali-free aluminum-boron-silicate glass ("E" glass) or alkali containing glass ("C" glass) can be used, as well as others. Preferred is a ground short glass fiber.

Any of the hydrogen polysiloxanes known in the art can serve as component (c). Especially useful are those those set forth by formula in U.S. 3,971,756. The patent also cites U.S. 2,445,794; 2,448,756; 2,484,595 and 3,514,424 as showing ways of making such siloxanes. To save unnecessarily detailed description, these are all incorporated herein by reference. Most important members of the family are those in which R is methyl, or phenyl, or a mixture thereof. These are commercially available. At the present time, it is preferred to use poly(methyl hydrogen)siloxane, a fluid which is available commercially from General Electric Company under the trade designation DF-1040.

In some embodiments, it is contemplated to use a small amount, e.g., up to 10 parts by weight per 100 parts by weight of (a), (b) and (c) combined, of an impact modifier. This can comprise a polyacrylate, or a copolymer of a diene and acrylonitrile and/or vinyl aromatic compound. A preferred such modifier is a block copolymer, of the linear or radial type, comprising diene rubber center blocks and vinyl aromatic terminal blocks. Illustrative dienes are butadiene or isoprene, and illustrative vinyl aromatics are styrene, vinyl toluene, and the like. Especially suitable are selectively hydrogenated such compounds. Particularly valuable are the selectively hydrogenated linear ABA types, made from styrene (A) and butadiene (B), and sold by Shell Chemical under the tradename

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Kraton G, and the corresponding radial teleblocks sold by Phillips Chemical under the tradename Solprene.

Any conventional method can be used to formulate the present thermoplastic compositions, and to mold them. The important factor is to insure intimate admixture. The amount of components (a), (b) and (c) and, optionally (d) to be used have been broadly set forth above. Preferably, however, the siloxane will be present in an amount of from about 0.05 to less than 0.5, and especially preferably, about 0.4 parts, by weight per 100 parts by weight of (a), (b) and (c) combined. Especially preferably the fibrous reinforcing agent will be present in an amount of from about 15 to about 40 parts by weight per 100 parts by weight of (a), (b) and (c) combined. Mixing temperatures and molding temperature will be illustrated in the following examples, but, in any event, will be entirely in harmony with those well known to those skilled in the art of polyester resin technology.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following example illustrates the compositions of the present invention. It is not to be construed to limit the claims in any manner whatsoever.

EXAMPLE 1

A polyester composition was prepared by extruding poly(ethylene terephthalate), short milled glass fibers essentially free of any sizing agent and, where indicated, a polymethyl hydrogen siloxane (DF 1040, General Electric Comapny). Extrusion is carried out at 265°C. and the extrudate is comminuted into pellets.

The pellets are then injection molded at about 300°C. (cylinder) into standard physical test specimens, so that heat distortion temperature (HDT) can be measured according to standard test methods; Izod impact strength, notched and unnotched can be measured on 1/8" bars according to standard test methods; elastic modulus and tensile

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yield strength and elongation at yield and at break can be measured according to standard test methods.

The compositions used, and the properties observed are set forth in Table 1:

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TABLE 1

Short Fiber Reinforced Polyester Compositions

<u>Compositions (parts by weight)</u>		<u>Example A</u>	<u>Example B</u>
	Poly(ethylene terephthalate)	80	80
10	Poly(methyl hydrogen siloxane) ^a	--	0.5
	Short unsized glass fibers ^b	20	20
<u>Properties</u>			
	Melt viscosity, 300°C. Pa-s	310	390
	Heat Distortion Temperature, °C.	75	75
15	Tensile Modulus, N/mm ²	4200	3910
	Tensile Strength, N/mm ²	69.5	60.5
	Elongation at break, %	3.5	14
	Time to failure in gasoline at 1% strain	No failure in 20 hours	
20	Whitening in gasoline	No	No
	Izod impact:		
	notched, J/m	35	65
	unnotched, J/m	350	950
	Falling dart impact, J.10 Kg; h = var;	5	80
25	φ 10 cm disc; w = 3.2 mm φ 9.5 cm ring support		

^a DF 1040, General Electric Company

^b EC 10W, Gevetex Co.

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Obviously many variations are possible in light of the above detailed description. For example, the poly(ethylene terephthalate) can be substituted with poly(1,4-butylene terephthalate). The poly(methylhydrogen)siloxane can be substituted with a poly(phenylhydrogen)siloxane.

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Instead of short glass fibers, unsized long glass fibers can be substituted. An impact improving amount, e.g., 5% by weight of a selectively hydrogenated block copolymer of styrene-butadiene-styrene, e.g., Shell's Kraton G, can be included in the composition. All such obvious variations are within the full intended scope of the appended claims.

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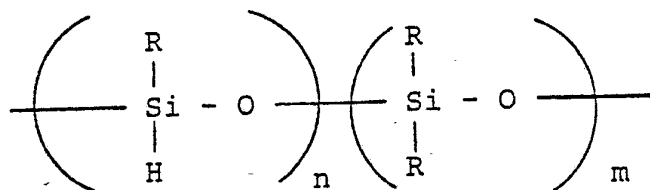


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CLAIMS

1. A high impact strength, high modulus thermoplastic composition comprising, per 100 parts by weight (a), (b) and (c), and intimate admixture of:

- 5 (a) from about 35 to about 95 parts by weight of a linear polyester;
- (b) from about 5 to about 65 parts by weight of a fibrous reinforcing agent essentially free of any sizing agent; and
- 10 (c) from about 0.05 to about 4 parts by weight of a hydrogen siloxane comprising units of the formula



15 wherein R is hydrogen, C₁-C₁₀alkyl, phenyl, or a mixture of any of the foregoing, and n plus m is at least about 4.

2. The composition of claim 1 wherein the siloxane is present in an amount of from about 0.05 to less than about 0.5 parts by weight per 100 parts by weight of (a), (b) and (c) combined.

3. The composition of claim 1 wherein the siloxane is present in an amount of about 0.4 parts by weight per 100 parts by weight of (a), (b) and (c) combined.

4. The composition of claim 1 wherein the linear polyester is poly(ethylene terephthalate).

5. The composition of claim 1 wherein the linear polyester is poly(1,4-butylene terephthalate).

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6. The composition of claim 1 wherein the fibrous reinforcing agent comprises glass fibers or rockwool fibers.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US 83/00636

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ³ : C 08 L 67/02 //(C 08 L 67/02, 83/04), C 08 K 7/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC ³	C 08 L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	WO, A, 8000255 (GENERAL ELECTRIC) 21 February 1980 see claims 1-13 ---	1-6
Y	DE, A, 2853882 (GENERAL ELECTRIC) 5 July 1979 see claims 1-15 -----	1-3
* Special categories of cited documents: ¹⁵ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
11th January 1984	07 FEB. 1984	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
EUROPEAN PATENT OFFICE	G.L.M. Kruidenberg	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 83/00636 (SA 5253)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 20/01/84

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A- 8000255	21/02/80	EP-A- 0016123	01/10/80
		CA-A- 1148291	14/06/83
DE-A- 2853882	05/07/79	JP-A- 54102351	11/08/79
		US-A- 4221728	09/09/80
		CA-A- 1119739	09/03/82

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